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SOME PROPERTIES OF
IONIC CRYSTALS

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INAUGURAL DISSERTATION

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BY

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Papers summarized in the dissertation

1. S. O. LUNDQVIST, A quantum mechanical investigation of the binding energy of the LiH-crystal. *Ark. Fys.*, 8, 177 (1954).
2. S. O. LUNDQVIST, On the elastic constants of cubic ionic crystals. *Ark. Fys.*, 6, 25 (1953).
3. S. O. LUNDQVIST, On the limiting vibrational frequencies of a cubic ionic lattice. *Ark. Fys.*, 9, 435 (1955).

A Study of Some Properties of Ionic Crystals

This investigation is concerned with the quantum mechanical treatment of simple ionic crystals with ions having complete electron shells. The starting point is the previous treatments of ionic crystals by HYLLERAAS, LANDSHOFF and LÖWDIN in the Heitler-London approximation. HYLLERAAS formulated the physics of the problem and derived the energy expression for the LiH crystal. LANDSHOFF introduced the convenient calculating device of using approximately ortho-normalized one-electron wave functions, obtained as linear combinations of the atomic orbitals. Later LÖWDIN found a mathematically exact method of ortho-normalisation and derived the corresponding expression for the energy. In his numerical applications, however, he did not use this expression, which is rather complicated, but introduced a series expansion in the overlap integrals and considered an approximation similar to LANDSHOFF's, taking some more terms into account. In the treatments by HYLLERAAS and LANDSHOFF the energy was considered as a function of the interionic distance only. LÖWDIN extended the treatment to the case of a homogeneously deformed lattice and derived formulas for the elastic constants. He pointed out that the overlap of the atomic wave functions introduces interaction terms corresponding to a rather complicated many-body potential. He also computed the elastic constants for several alkali halides taking such terms into account. The calculated values agree rather well with the empirical results; the deviations from the Cauchy relations have the correct sign, but are too large.

The first paper (1) is concerned with the calculation of binding energies with numerical applications to the LiH crystal, formerly treated by HYLLERAAS. In a preliminary investigation¹ it was found that certain approximations which had proved successful in the treatment of other simple ionic crystals, e.g. NaCl and KCl,

¹ S. O. LUNDQVIST and P. O. FRÖMAN, Some remarks on the calculation of the cohesive energy of ionic crystals. *Ark. Fys.*, 2, 431 (1950).

did no longer seem to be valid in the case of LiH. In particular the expansion of the binding energy in terms of the overlap integrals, which had been used in the earlier investigations, did not even seem to converge in the case of LiH. Therefore a new investigation of LiH was undertaken with LÖWDIN's expression for the energy as the starting point. Because of the large spatial extension of the hydrogen ion wave functions it seemed necessary to consider the overlap between neighbours up to the sixth order. The expression for the energy of the crystal contains sums of three-centre and four-centre integrals, which were neglected in the earlier investigations. The calculation of such integrals presents considerable difficulties and they have not yet been completely investigated. Due to the tremendous number of such integrals occurring in our calculation, we had to compute them by approximate methods.

In order to make a comparison with the approximations used earlier the binding energy was computed also in the approximation where the energy is expanded in terms of the overlap integrals and all terms which are small of third and higher orders are neglected. This calculation was done in three successive stages of approximation. The method of dividing the energy expression into terms of various orders of smallness and neglecting quantities of third and higher orders has no rigorous meaning in the case of LiH but, nevertheless, we found that the binding energy in all three stages of approximation agreed very well with that computed according to LÖWDIN's energy formula.

The agreement between the calculated and the observed binding energy was not very good, the discrepancy amounting to about ten per cent. The reason probably is that the use of the wave functions for free hydrogen ions is a rather poor approximation. The wave functions for a free hydrogen ion tend to zero very slowly with increasing distance from the nucleus and accordingly we have to expect the occurrence of considerable changes in the lattice due mainly to the strong fields of the surrounding positive ions. We tried to get an estimate of this effect by regarding the effective nuclear charge of the hydrogen ion as a variable parameter and minimizing the total energy of the crystal. The variation removed about $\frac{1}{3}$ of the discrepancy between the calculated and the observed binding energy, but resulted in only a slight change of the effective nuclear charge.

The aim of this investigation has only been to make a more detailed investigation along the lines of the preceding papers. The result clearly indicates the importance of trying to improve the treatment in various respects. In the last few years great efforts have been made to develop convenient methods to calculate energies of molecules and crystals more accurately, and it may be hoped that an improved treatment of this problem will soon be possible.

A discussion of the elastic constants c_{12} and c_{44} , in particular the deviations from the Cauchy relation, is given in the second paper (2), supplementing the treatment earlier given by LÖWDIN. The discussion is restricted to cases where terms in the energy formula, which are small of third and higher orders in the overlap integrals

can be neglected. The expression for the energy of the crystal in this approximation contains, besides ordinary two-body interaction terms, also a term which represents the interaction between three particles. It is shown that this term depends on the relative size of the positive and negative ions as well as on the amount of overlap between them. For an idealized crystal, where the positive and negative ions are assumed to be of the same size, it is shown that the three-body term vanishes, and hence the Cauchy relation is satisfied. It follows from the discussion in (2) that large deviations from the Cauchy relations are to be expected only for crystals where the positive ions are considerably smaller than the negative ones. Unfortunately the elastic constants have been measured at low temperatures only for very few ionic crystals, but the empirical results available seem to confirm the theoretical conclusion.

New formulas for the three-body potential and the elastic constants c_{12} and c_{44} have been derived, which take explicitly into account the effect of the asymmetry in size of the ions. A numerical application to NaCl showed a very close agreement with LÖWDIN's result concerning c_{12} and c_{44} , but we found a somewhat smaller value for the three-body potential. The treatment of the elastic constants in this approximation seems to provide a qualitatively satisfactory theory for the deviations from the Cauchy relations for certain simple ionic crystals. In order to obtain a good quantitative agreement the treatment has to be improved.

The last paper (3) is concerned with the vibrations of an ionic lattice, particularly the infra-red ones. The vibrations of a crystal are usually treated by expanding the potential energy in terms of the absolute displacements of the nuclei from their equilibrium positions. A more natural method, which was first applied to a general potential by WALLER, is to expand the potential energy according to powers of the relative displacements of the nuclei. The treatment of the elastic constants and the normal vibrations of a lattice according to this method has been given by WALLER. For the special case of the infra-red vibrations WALLER's general formula for the potential energy can be reduced to the simple form, which was derived long ago by BORN for the case of central forces. The potential energy for small displacements can then be written as a sum of interaction terms between pairs of ions even for the case of a many-body potential.

The vibrations of an ionic lattice have up to now been investigated essentially only on the basis of the classical theory by BORN. Here we have instead considered the approximate expression for the binding energy, in which terms small of third and higher orders in the overlap are neglected. The formula for the three-body potential derived in (2) proved to be unnecessarily complicated and it was possible to find a simple approximate formula, which seems to be sufficiently accurate for the purpose of this investigation. This simple formula made it possible to relate the frequencies to well-known measurable quantities, the elastic constants and the interionic distance.

The three-body term in the potential energy modifies both the repulsive and the

Coulomb term in the equations of motion, the modification of the Coulomb term being equivalent to replacing the actual ionic charge by an effective charge. The deviation of the effective from the actual ionic charge can be interpreted as due to the finite extension and deformability of the ions.

Formulas are derived for the frequencies of transverse and longitudinal vibrations of long wavelength. Since no allowance is made for the polarizability of the ions in the formula for the potential energy, this implies the neglect of the effect of the optical polarisation. In order to estimate the importance of the optical polarisation more accurate formulas were derived in which the polarisation was treated semi-empirically. A numerical comparison for NaCl and KCl shows that the neglect of the optical polarisation seems approximately justified for the transverse vibrations but is a rather poor approximation for the longitudinal waves; the ratio between the longitudinal and transverse frequencies being too high.

The treatment in (3) is valid at the absolute zero of temperature in the absence of the zero-point motion of the nuclei. To a certain approximation, however, the results are valid also at higher temperatures. Thus at room temperature the theoretical values for the transverse frequencies agreed within 4 per cent with the empirical values for NaCl and KCl.

This investigation has been carried out at the Institute of Mechanics and Mathematical Physics at the University of Uppsala. I wish to express my sincere gratitude to my teacher, Professor IVAR WALLER, for suggesting the subject of this thesis to me. During my years as his student he has given me most generously of his always valuable advice and outstanding instruction, and he has shown me the greatest kindness and encouragement. I am also indebted to Drs. P. O. FRÖMAN, P. O. LÖWDIN and A. SJÖLANDER for many stimulating discussions on various parts of my work.

